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► To cite this version:

Patrick Navard, Céline Cuissinat. Cellulose swelling and dissolution as a tool to study the fiber structure. 7th International Symposium "Alternative Cellulose: Manufacturing, Forming, Properties", Sep 2006, Rudolstadt, Germany. 7 p. hal-00579326

HAL Id: hal-00579326

<https://hal-mines-paristech.archives-ouvertes.fr/hal-00579326>

Submitted on 23 Mar 2011

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Cellulose swelling and dissolution as a tool to study the fiber structure

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The swelling and dissolution mechanisms of cotton or wood fibers cellulose fibers in aqueous (as N – methylmorpholine N-oxide and water mixtures, or soda solutions) or in ionic liquids are studied. Some cellulose samples treated by enzyme mixtures are investigated too. Six dissolution modes are found and detailed. The swelling (homogeneous or by ballooning) is the precursor of the dissolution step, which occurs by bursting of balloons or by unwinding of cellulose structure. These phenomena are due to morphological structure of the native cellulose fibres. The balloons formation reveals the elasticity and semi – permeability of primary and S1 layers, which play the role of a membrane. The intern stresses frozen during biosynthesis are revealed by unwinding. The study allows the influence of the solvent quality on the dissolution mechanism.

Key words: cellulose, swelling, dissolution, N – methylmorpholine N-oxide, ionic liquids, structure;

1. Introduction

Cellulose is the major constituent of plant cells and is present in most of them. Cotton and wood cell walls are usually composed of several well known layers or walls that depend on how the plant cells grow ⁽²⁾. Whatever the origin of the native fiber cells, some common morphological architecture can be recognized. In the outer layer, the so – called primary wall (P), fibrils of about 10 nm in diameter are positioned crosswise to a layer of about 50 nm thickness. The secondary wall (S) consists of two layers S1 and S2. The thickness of the S1 layer is, in the case of cotton, about 100 nm and in the case of spruce pulp fibre, about 300 nm. The fibrils are aligned parallel and densely packed into a flat helix, which may be in the opposite direction in subsequent S1 layers.

A large part of cellulose chemistry, physics and technology deals with the swelling and the dissolution of native cellulose. Despite cellulose is the more abundant biopolymer produced on Earth and that it may be of greater and greater importance over the next years, a lot of important questions still have to be understood. The first deals with the mode of biosynthesis of the vegetable cell where cellulose is mixed with other polysaccharides and substances. Another is the exact organization of the cellulose structures among natural substances and the origin of its variability. Finally, a question of scientific and technological importance is the way cellulose is dissolved.

The swelling of native cellulose in various solvents have been the subject of numerous investigations, most of them being confined to a crude description of the phenomena and a measure of the swelling ratio. The heterogeneous swelling of native cellulose fibres in the form of balloons scattered along the fibre was observed long ago in chemicals like sodium hydroxide/water or a mixture of N – methylmorpholine N-oxide (NMMO) and water. There were several tentative explanations for this phenomenon. For example OTT et al. ⁽³⁾ considers that during swelling in a solvent, the primary wall, considered as poorly soluble, cracks, then slides along the fiber to form protective regions where the cellulose cannot swell.

The focus of this work is to describe the swelling and dissolution mechanisms of native cellulose fibers (cotton and wood), in various range of solvents. Owing to the solubility of varying the

solvent quality, we are able to propose a systematization of the different dissolution modes, largely influenced and determined by the structure of cellulose fibers. The biosynthesis of cellulose fibers and, thus its morphological architecture, play a main role in the interactions with external agents as swollen or solvent systems.

2. Experimental part

2.1. Samples.

Three native fibers, one bleached cotton and two wood fibers, Buckeye VFC (pine wood pulp obtained after a treatment by vapor hydrolysis, the cooking occurred in a sodium sulfite and soda solution) and Borregaard VHF (fir tree pulp obtained by process with calcium bisulfite) have been used. These samples were treated (in collaboration with Lenzing, Austria, T. Röder) with an enzyme mixture of cellulase and xynalase to obtain cotton and wood cellulosic fibers without outer layers. A peeling rate, the percentage of solubilized sugars analyzed in the supernatant by electrophoresis per fiber weight, characterizes the treated cotton and wood samples. A peeling rate at 10% is giving a cellulose fiber without primary and part of secondary wall. The characteristics of samples are given in figure 1.

	Bleached cotton		Buckeye VFC		Borregaard VHF	
Peeling rate (%)	0	10.00	0	9.41	0	11.26
Cristallinity (%)	55	57	46	47	43	48
Mn (* 1000) (g/mol)	262.9	172.1	63.9	53.8	152.6	115.8
Mw (*1000) (g/mol)	606.3	512.3	121.1	114.1	766.7	449
Mz (* 1000) (g/mol)	998.4	907.8	215.2	216.1	1600.5	1411.5
w (DP < 50)	0.1	0.3	0.3	0.7	0.3	0.6
w (DP < 200)	1.1	2.9	9.3	14.2	4.7	6.0
w (DP > 2000)	68.1	57.9	4.7	4.9	63.1	51.9

Figure 1: Properties of (untreated and treated by enzyme mixtures) cotton and wood samples

2.2. Solvent systems

The swelling and dissolution treatments are performed in the following solvents:

- aqueous systems: N-methylmorpholine n-oxide (NMMO) and water (with various content of water, from 17 to 45% of water, w/w) or sodium hydroxyde (NaOH) solution at 7.6%.
- non-aqueous systems: mixture of lithium chloride (LiCl) and dimethylacetamide (DMAc)
- ionic liquids: Glycolic acid (99%), and –N-butyl-3-methylimidazolium chloride (noted [C₄mim]Cl), allylmethylimidazolium bromide (noted CP040) and butenylmethylimidazolium bromide (noted CP041). The ionic liquid [C₄mim]Cl is a cellulose solvent. CP040 and CP041 are known only as swelling agents of cellulose. These swelling and dissolution experiments were performed at the Centre of Excellence for Polysaccharide Research at the University of Jena, Germany, with Prof T; Heinze.

The experimental temperature varies as a function of solvent systems used (around 90 °C for NMMO – water mixtures and ionic liquids, -5 °C for NaOH solutions).

2.3. Observations by optical microscopy

Cellulose and solvent were mixed in a container made of two glass plates. No agitation was applied to the system. About ten fibers were placed between the two glass plates. The fibers can move freely between them. Only one extremity of cellulose fibers is fixed on the plate in order to avoid the fiber to be too much affected by solvent convection, which is causing difficulties for the optical observations. The solvent contained in a pipette was introduced by capillary forces between the two plates.

The swelling and dissolution of cellulose fibers were observed by optical microscopy with a Metallux 3 (Leitz) equipped with a Linkam TMS 91 hot stage. The samples are investigated in transmission mode.

3. Results and discussion

3.1. Different dissolution modes.

Five mechanisms can be observed when a cellulose fiber (cotton or wood) is placed in fluid materials:

- mode 1: fast dissolution by disintegration into fragments (e.g. cotton or wood fibers in NMMO – water at 17%)
- mode 2: large swelling by ballooning, and dissolution (e.g. cotton or wood fibers in NMMO – water mixtures, from 19 to 23% in water content; and in ionic liquid [C4mim]Cl)
- mode 3: large swelling by ballooning, and no dissolution (e.g. cotton or wood fibers in NaOH 7.6%-water)
- mode 4: homogeneous (weak or low) swelling, and no dissolution (e.g. treated and untreated in ionic liquids CP040 and CP041, or cotton and wood fibers in NMMO– water above 45% in water content)
- mode 5: no swelling, no dissolution

The behaviour varies with the quality of solvent which decreases from mode1 to mode 5.

We describe each dissolution mode in the following part. The first explained mode is the mode 2 (swelling by ballooning and dissolution) because it is considered as the reference mode. A complementary study on the mechanism by homogeneous swelling and dissolution by unwinding is presented. This work is based on experiments with treated cotton and wood fiber with a peeling rate at 10% in NMMO – water mixture, from 19 to 23% in water content, or in NaOH 7.6%-water

3.2. Mode 1: fast dissolution by disintegration into fragments.

Below 17% of water in NMMO-water mixtures, the cotton and wood fibres are readily dissolved. Figure 5 shows the disintegration of wood fibres into a series of spindle ⁽⁴⁾. No appreciable swelling occurs before the disintegration of fibres structure. The bursting into fragments of cellulose fibres takes place as of the introduction of solvent systems. The cellulose fibres are broken over all their length and burst into fragments

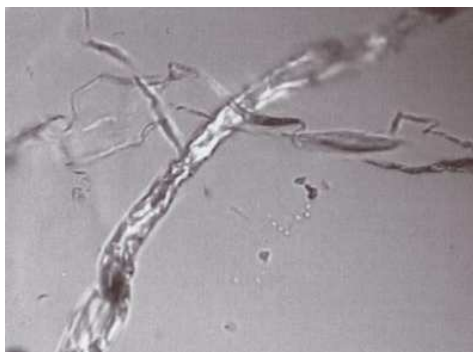


Figure 5: wood fibre (Borregaard) swollen in NMMO – water at 17%

3.3. Mode 2: Swelling and dissolution mechanism via ballooning.

The swelling of native cellulose cotton and wood fibers is not homogeneous along a fiber in NMMO-water mixtures or soda solutions or LiCl – DMAc systems. Only some selected places undergo swelling. This localized swelling gives the impression of having balloons growing. This phenomenon (called ballooning) is followed by the dissolution of the fibers. The ballooning effect of cellulose fibers has attracted a lot of attention due to its spectacular appearance and its quite intriguing effect ⁽⁴⁾.

The fibers having a rather regular diameter in a dry state start to swell at given isolated points along the fiber. The zones where the swelling starts increase in size (Figure 2). The fiber has a series of swollen

transparent parts, of rounded shape, that we will call balloons. These balloons are growing and reaching a maximum size at which they will burst. We can distinguish different zones within one fiber during the ballooning (seen in Figures 2 and 3). These various zones are defined as follows: an unswollen fiber (A), a balloon (B), cellulose swollen then dissolved inside the balloon and membrane (C). Ballooning and dissolution phenomenon are the same for cotton and wood fibers whatever the solvent agent is (NMMO – water from 19 to 23% in water content, ionic liquid $[C_4mim]Cl$ or $LiCl - DMAc$). Thus, ballooning effect and dissolution mode can be only due to the way these cellulose fiber are morphologically structured.

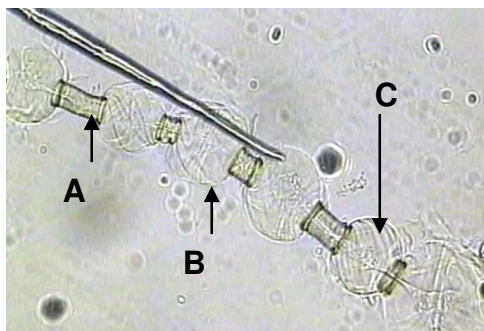


Figure 2: Wood fiber (Buckeye VFC) in NMMO – water (20%)

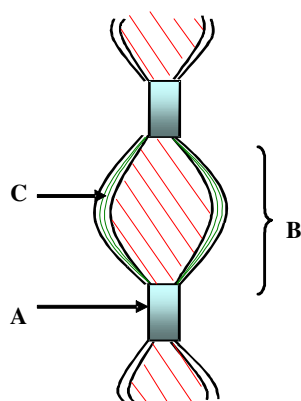


Figure 3: Schematic drawing of a swollen fiber of native cellulose

All the studied fibers are following the same sequence of events from the start of swelling to the complete dissolution. Swelling and dissolution take place for cotton and wood fibers in four subsequent phases.

- Phase 1 = appearance of balloons along the fibers: after the introduction of the solvent, we observe the appearance of balloons along the fibers. The time needed for their formation depends on the type of native fibers. The balloons do not appear at the same time along the fiber. The balloons give the aspect of a beaded structure, with the beads distributed in more or less regular way depending on the type of native fibers. Balloons do not present a regular circular perimeter. The border shape of the balloon is defined by a kind of ribbon surrounded the balloons (Figure 4). This helical structure can be seen as lines going from one unswollen zone to the next with one turn.

- Phase 2 = bursting of balloons: the balloons continue to swell until they reach a maximal swelling ratio. They remain in this swollen state a certain time (that again depends on the type of native fibers) and then burst. When the membrane (C) burst, the liquid contained inside moves out very quickly. This phenomenon is not simultaneous for all the balloons along a given fiber. Balloon bursting is due to the increase of the osmotic pressure inside the balloon. The scraps of the balloon membrane (C) remain attached to the unswollen sections (A) of the fibers. Another important point is that the inside of the balloon is very fluid at the time of the bursting since it flows out very rapidly. Thus the viscosity should be small which means that cellulose inside the balloon is not a gel but is dissolved.

- Phase 3: dissolution of the unswollen sections (A). This dissolution begins at the section surface (and not at the two extremities) and goes on to the fiber centre.

- Phase 4: dissolution of the balloon membrane scraps: during this last stage, the scraps of the balloon membrane also dissolve.

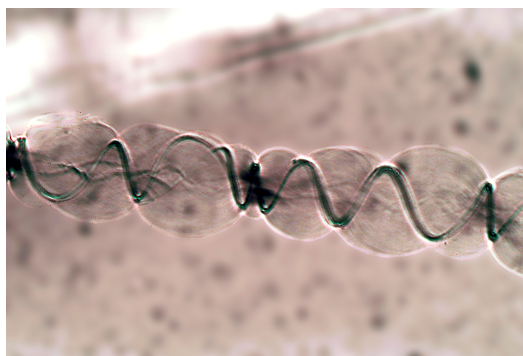


Figure 4: Bleached cotton in NMMO – water (20%)

The formation of balloons is an intriguing effect. One obvious question is about the origin of the balloon membrane. It can be explained by studying the structure of the cellulose outer layers and by the experiments carried out with enzymatically treated cotton and wood fibers. Indeed, when performing peeling of a few percent of the outside surface of the cotton or wood fibers, swelling and dissolution occur without ballooning (cf mode 3), homogeneously along the fibers. What we called membrane is thus a fraction of the fiber that can not be dissolved easily and it is semi-permeable and fairly elastic. The experiments performed with treated samples suggest that the membrane resisting dissolution is the primary wall plus all or a fraction of the S1 layer (usually shown with a helical structure).

3.4. Mode 3: large swelling by ballooning, and no dissolution

In the case of cotton or wood cellulose in NMMO – water (at water content between 25 and 35%) mixture or in NaOH (at 7.6%) solutions, the swelling occurs by ballooning, but dissolution never occurs ⁽⁵⁾. The phase 1, ever described in dissolution mode 3, takes place but the dissolution steps are never reached by these solvents. In fact, the balloons are growing up to a certain diameter that is controlled by the quality of the solvent and the extension resistance of the membrane. For solvents like the NMMO-water between 25 and 30%, the growth is stopped probably because the resistance of the membrane exceeds the osmotic pressure of the solvent that wishes to dilute the cellulose solution. When the solvent is good enough (NMMO-water at 19, 20 and 23%), its penetration through the membrane is not stopped by the mechanical resistance of the membrane and it continues to enter the balloon to dilute cellulose, thus increasing the expansion of the membrane up to its bursting.

3.5. Mode 4: homogeneous (weak to very low) swelling and no dissolution

The cotton and wood fibres swell homogeneously in NMMO-water mixtures with high water content (higher than 35%) or in ionic liquid (CP040 and CP041) ^(4, 7). Increasing water content in NMMO-water solvent systems decreases the ability of this mixture to dissolve cellulose. The diameter of native cellulose fibres increases as of the introduction of NMMO-water solutions. The ratio of diameter of swollen fiber by diameter of dried fiber varies between 2.3 and 2.6 for cotton, Borregard and Buckeye fibers. Thus the swelling is low. The fibers stay in this swollen state; they are never dissolving.

3.6. Mode 5: no swelling, and no dissolution

It is the case of non solvents.

3.7. complementary study: Homogeneous swelling and dissolution by unwinding of structure fibers.

The enzymatically treated cotton and wood fibers ⁽⁶⁾ homogeneously swell in aqueous solvents or ionic liquid [C4mim]Cl. No balloon appears during the swelling step. Then they are dissolved. The dissolution occurs by the unwinding of the fibers structure. This step precedes the dissolution phase. The swelling and dissolution mechanisms for the treated fibers can be divided in 3 phases:

- Phase 1: homogeneous swelling of the treated fibers. The treated cotton and wood fibers swell along all its length. The homogeneous swelling is weak. Contrary to the swelling and dissolution mechanism observed in the case of cotton and wood cellulose fibers, the swelling does not occur via ballooning.

- Phase 2: unwinding of the treated cotton and wood fibers. Once the treated cotton and wood fibers are swollen, a unwinding of its structure occurs. The treated cellulose fibers turn on themselves and every fiber is separated in sub-fibers.

- Phase 3: dissolution of the cellulose fibers. The sub-fibers are disintegrated into fragments. Then these fragments are dissolved. Not all the solvent agents reach this last step of dissolution. It depends on its ability to develop interactions with cellulose fibers. The unwinding of structure is a phenomenon particularly interesting to study. The unwinding of treated cotton and wood fibers occurs as describing below. Every treated fiber undergoes a left handed untwisting, which ends up at its separation in sub fibers. Once the fibers are swollen, an intern helical structure is observed and progressively turns on itself. This untwisting can only be due to the release of internal stresses frozen during the biosynthesis of fibers. As the treated cellulose fibers release their internal stresses, the pitch of the helical structure increases (Figure 6). The unwinding of structure is fast. The pitch of the helical structure is at least multiplied by 2 during unwinding. This study seems to support that a unwinding of the helical structure of the fibre is necessary for moderately good solvents to dissolve cellulose.

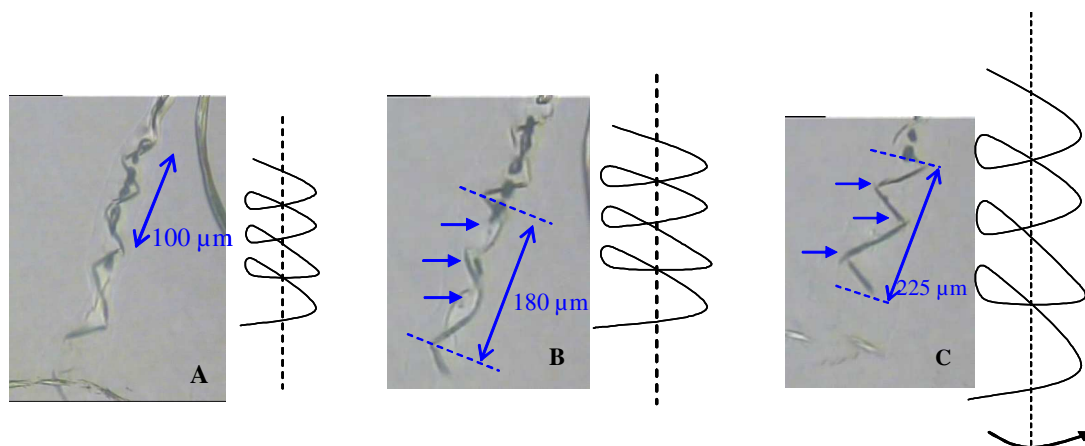


Figure 6: Untwisting of treated cellulose fiber (treated cotton wood fiber, peeling rate = 10%) in NMMO – water solution at 20%. Pictures A, B and C are respectively associated to the time 5 min 25s, 5 min 46s and 6 min. The drawing illustrates the increase of the pitch of helical structure

4. Conclusion

Using a wide range of solvents, and in particular not very good solvents, we were able to identify several dissolution modes. The main results of this study are the fact that the helical structure that is present in wood and cotton fibres plays a role in dissolution. The balloons are a location where unwinding of the structure occurs in the balloon while the helical arrangement of the fibrils is still present in the unswollen part. Only the region that was able to unwind can be dissolved. The same occurs for peeled samples, where the unwinding precedes the dissolution. A second important result is the fact that if an unwinding occurs, it means the system is going back into a more thermodynamically stable state. This implies that the helical structure is built

under stress, this stress being released when a solvent enters the fibres and allows the fibrils to move.

The last results of this study deals with the ballooning effect. It shows that the outside of the fibre (primary wall plus part of the secondary wall) is not as soluble as the inside of fibre. Whether this is due to its composition or to the fact that it is still in a helical configuration remains to be found

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